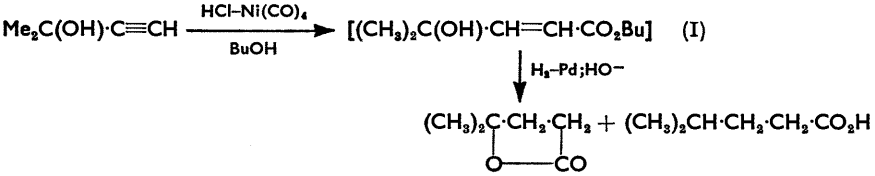
930. *Researches on Acetylenic Compounds. Part LVII.* A General Synthesis of Allenic Acids.*

By E. R. H. Jones, G. H. Whitham, and M. C. Whiting.

The reaction between 2-methylbut-3-yn-2-ol, nickel carbonyl, and hydrogen chloride gives the ester of a conjugated allenic acid as the main product and involves the corresponding acetylenic chloride as an intermediate. Analogous chlorides of widely varying substitution patterns react similarly with nickel carbonyl, giving a range of allenic acids by a simple and convenient procedure.

Parts XXII[1] and XXIX[2] of the present Series describe the reactions of nickel carbonyl with mono- and di-substituted acetylenes, respectively, from a preparative standpoint, while Parts XXX[3] and XXXI[4] discuss the stoicheiometry of the reaction and some complexities (inhibition and catalysis) of its mechanism. Bergmann and Zimkin[5] have described a reaction between 2-methylbut-3-yn-2-ol, nickel carbonyl, anhydrous butanol, and hydrogen chloride, which was formulated as follows:



$$Me_2C(OH){\cdot}C{\equiv}CH \xrightarrow[BuOH]{HCl-Ni(CO)_4} [(CH_3)_2C(OH){\cdot}CH{=}CH{\cdot}CO_2Bu] \quad (I)$$

$$\downarrow H_2\text{-}Pd;HO^-$$

$$(CH_3)_2\underset{|}{C}{\cdot}CH_2{\cdot}\underset{|}{CH_2} \;(O\text{——}CO) + (CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

The main fraction of the reaction mixture was a heterogeneous liquid believed to be essentially the ester (I). It was hydrogenated over palladium, then hydrolysed, separation of acidic and neutral products giving γ-methylvalerolactone and γ-methylvaleric acid in unstated yields. *Prima facie* evidence was thus adduced for a reversal, under these conditions, of the direction of addition of $H \cdots CO_2H$ to the acetylenic bond proved by Reppe *et al.*[6] for simple monosubstituted acetylenes and assumed in Part XXII of this Series.[1] To clarify the situation it was necessary to find which of the changes in molecular structure and reaction conditions were responsible for this reversal, particularly since some features reported by Bergmann and Zimkin were ambiguous or unexpected. The evidence for the primary product (I) was inconclusive, especially since the postulated hydrogenolysis over palladium is inconsistent with the work of Haynes and Jones.[7]

The experiment was therefore repeated essentially as described; a main fraction was obtained with physical constants close to those reported. On careful fractional distillation two homogeneous substances were separated (from appreciable amounts of higher-boiling materials of still unknown constitution) and identified as the known lactone (II), and the allenic ester (III). The latter was hydrolysed to the crystalline acid (IV), of which the structure follows from ultraviolet and infrared spectra, hydrogenation to γ-methylvaleric acid, and the production of acetone on ozonolysis. There is thus no need to assume the formation of the ester (I), since the hydrogenation products isolated by Bergmann and Zimkin were obviously derived from our products (II) and (III); indeed even the heterogeneous higher-boiling fractions could not have contained their ester (I) in quantity.

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* Part LVI, *J.*, 1957, 2597.

[1] Jones, Shen, and Whiting, *J.*, 1950, 230.

[2] *Idem, J.*, 1951, 48.

[3] *Idem, J.*, 1951, 763.

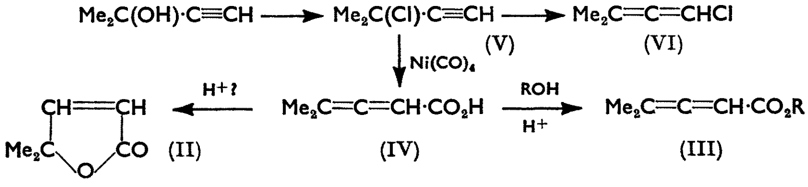
[4] *Idem, J.*, 1951, 766.

[5] Bergmann and Zimkin, *J.*, 1950, 3455.

[6] Reppe (and his collaborators), *Annalen*, 1953, **582**, 1.

[7] Haynes and Jones, *J.*, 1946, 954.

Further investigation showed that 2-methylbut-3-yn-2-ol is probably not directly involved in the reaction with nickel carbonyl. In the reaction conditions used, it would be converted rapidly (if reversibly) into the chloride (V); just possibly this might be isomerised to the allene (VI) in the presence of nickel chloride.[8] These chlorides were therefore prepared and treated with nickel carbonyl in aqueous-methanolic acetic acid. The allene (VI) failed to react, but (V) gave the ester (III; R = Et) in fair yield. When sodium acetate was added in excess so that nickel chloride, a Lewis acid and an efficient esterification catalyst, could not be formed, the free acid (IV) was the main product. The neutral fraction contained the ester (III; R = Et) and a small quantity of lactone (II); the yield of the latter was much smaller than in the original experiment starting with 2-methylbut-3-yn-2-ol. We believe that the reason for the difference in the yield-ratio for the lactone and allenic acid derivative is trivial rather than fundamental, *i.e.*, that the former is formed from the allenic acid under the catalytic action of the acidic species present, rather than that the alcohol itself is involved in a reaction with nickel carbonyl, leading directly to the lactone. This view is supported indirectly by the isomerisation of 2-butylbuta-2 : 3-dienoic acid (see below) to the lactone of 2-butyl-4-hydroxybut-2-enoic acid when an attempt was made to distil a sample *in vacuo.*



Under Bergmann and Zimkin's conditions, 1-ethynyl*cyclo*hexanol, prop-2-yn-1-ol, and 1 : 1-diphenylprop-2-yn-1-ol failed to give significant quantities of isolable reaction products with nickel carbonyl, although the last alcohol was converted into a non-crystalline and undistillable deeply coloured syrup, from which no acidic compound was obtained on hydrolysis. 3-Methylpent-1-yn-3-ol, on the other hand, underwent a reaction analogous to that of its lower homologue. This is the only alcohol of the four which readily yields a chloride on treatment with hydrogen chloride.

As a route to an allenic acid, the reaction of a chloride of the type (V) with nickel carbonyl in buffered aqueous ethanol compares favourably with the alternative method described by Wotiz,[9] in which the derived Grignard reagent is treated with carbon dioxide and the resulting βγ-acetylenic and αβγ-allenic acids and a dimeric acid are separated, although with some experimental difficulty. The general reaction is: $R^1{\cdot}C{\equiv}C{\cdot}CR^2R^3Cl \longrightarrow HO_2C{\cdot}CR^1{:}CR^2R^3$, and several variants were therefore investigated in addition to the case $R^1 = H$, $R^2 = R^3 = Me$, described above. Six chlorides (with $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, $R^3 = Me$; $R^1 = R^2 = H$, $R^3 = Pr^n$; $R^1 = R^2 = H$, $R^3 = Ph$; $R^1 = Bu$, $R^2 = R^3 = H$; and $R^1 = Bu$, $R^2 = R^3 = Me$) gave the corresponding allenic acids, although in some cases yields were low, probably because isolation procedures were insufficiently mild for these somewhat unstable compounds. The method is thus general, and it renders αβγ-allenic acids as accessible as many more familiar conjugated dienes; in view of their great reactivity[10] they may be useful synthetical intermediates. The crystalline penta-2 : 3-dienoic acid thus obtained is one of the simplest possible resolvable allenes; its participation in prototropic rearrangements has already been discussed.[11]

Like the normal Reppe carboxylation, this variant can be written as a nucleophilic

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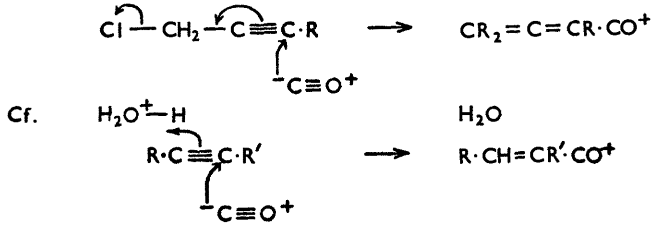
[8] Hennion, Sheehan, and Maloney, *J. Amer. Chem. Soc.*, 1950, **72**, 3542.
[9] Wotiz, *ibid.*, 1950, **72**, 1639.
[10] See, *inter al.*, Eglinton, Jones, Mansfield, and Whiting, *J.*, 1954, 3197.
[11] Jones, Whitham, and Whiting, *J.*, 1954, 3201.

addition of the $^{-}C{\equiv}O^{+}$ fragment, concerted in this case with displacement of Cl^{-} instead of addition of H^{+}:



In both reactions, however, it seems probable that the breakdown of an unstable metal complex involving carbon monoxide and the acetylene is involved; recently several such complexes have been described for other transition metals.[12] The stoicheiometry of this new variant has been investigated in a preliminary manner only. No acid is required (though acetic acid was in fact present in most of the experiments described), and the molar ratio $[Ni(CO)_4]$: [Chloride] : $[Cl^{-}$ formed] : [Allenic acid derivative] appears to be roughly 2 : 2 : 2 : 1.

FIG. 1. (1) *Buta-2 : 3-dienoic acid*; (2) *penta-2 : 3-dienoic acid*; (3) *4-methylpenta-2 : 3-dienoic acid*; (4) *2-butylbuta-2 : 3-dienoic acid*.

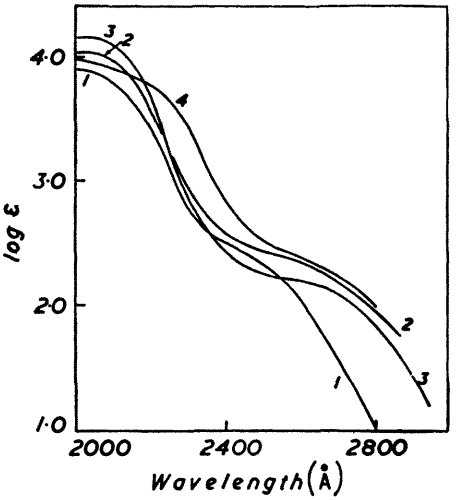
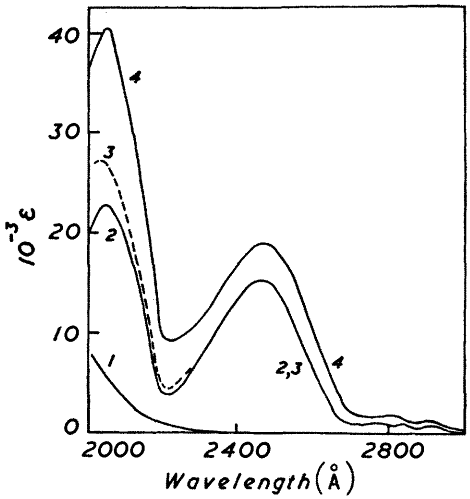


FIG. 2. (1) *Acrylic acid*; (2) *styrene*; (3) *summation curve for* 1 + 2; (4) *4-phenylbuta-2 : 3-dienoic acid*.



The ultraviolet absorption spectra of the allenic acids further confirm the simple generalisation of Celmer and Solomons[13] about allenes, that the two fragments separated by the central carbon atom of the allene grouping behave approximately as though insulated from each other. This is shown in Fig. 1 in the case of the simple αβγ-allenic acids which, like αβ-ethylenic acids, have a marked inflexion at about 2400—2600 Å, and in Fig. 2 for 4-phenylbuta-2 : 3-dienoic acid. In the latter the absorption of the allene is very similar to, but 30—50% more intense than, the sum of the curves for acrylic acid and styrene. Much of the vibrational fine-structure (benzenoid spacing of *ca.* 900 cm.$^{-1}$) in the spectrum of styrene is lost on passing to the allenic acid. Some qualification of the above generalisation is thus necessary.

The infrared spectra of allenic acids and esters have already been discussed by Wotiz

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[12] Reppe and Vetter, *Annalen*, 1953, **582**, 133; Sternberg, Greenfield, Friedel, Wotiz, Markby, and Wenders, *J. Amer. Chem. Soc.*, 1954, **76**, 1457.

[13] Celmer and Solomons, *ibid.*, 1953, **75**, 1372.

and Celmer,[14] with whose findings our results for the substances now described are in agreement. The intense doublet at about 1920 and 1970 cm.$^{-1}$ is a characteristic feature of acids of the type $H_2C{=}C{=}CR{\cdot}CO_2H$ and their derivatives; acids of types $R{\cdot}CH{=}C{=}CH{\cdot}CO_2H$ and $R_2C{=}C{=}CR{\cdot}CO_2H$ show a single band at 1960—1970 cm.$^{-1}$. An intense band at 850 cm.$^{-1}$ is observed in all compounds $R_2C{=}C{=}CH_2$, and is presumably attributable to the olefinic C–H out-of-plane deformation mode, which occurs at *ca.* 890 cm.$^{-1}$ in $R_2C{=}CH_2$.

EXPERIMENTAL

Reaction between Nickel Carbonyl and 2-*Methylbut*-3-*yn*-2-*ol*.—A mixture of butan-1-ol (150 c.c., containing hydrogen chloride, 40 g.) and 2-methylbut-3-yn-2-ol (84 g.) was stirred under nitrogen and warmed to 40° while nickel carbonyl (44 c.c.) was added dropwise during 2 hr. at such a rate as to maintain the temperature at about 65°. After cooling and removal of excess of nickel carbonyl by co-distillation with ether (100 c.c.) the residue was poured into water and extracted with ether. The acid fraction yielded an oil (0·5 g.) which solidified and crystallised from water as fine needles (0·13 g.), m. p. 59° (Found: C, 61·25; H, 8·6%; equiv., 209). Light absorption max. at 2210 Å ($E^{1\%}_{1\,\text{cm.}}$ 430). This acid was not investigated further. Careful distillation of the neutral fraction gave, after removal of butanol, homogeneous fractions: (i) (18·5 g.), b. p. 85—86·5°/12 mm., n_D^{20} 1·4443, and (ii) (32 g.), b. p. 64·5—65°/0·1 mm., n_D^{12} 1·4600, together with heterogeneous fractions of higher b. p.

Fraction (i) was identified as 4-hydroxy-4-methylpent-2-enoic lactone (17% yield) (Haynes and Jones [7] give b. p. 80°/10 mm., n_D^{18} 1·4470). Hydrogenation in ethyl acetate over platinum resulted in the uptake of 98% of the theoretical amount of hydrogen and gave the corresponding saturated lactone, b. p. 105° (bath)/16 mm., n_D^{20} 1·4249, m. p. *ca.* 2° (Noyes [15] gives b. p. 208°/760 mm., m. p. 7—8°), identified by conversion into 4-hydroxy-4-methylpentanamide, m. p. 99—101°, with aqueous ammonia (Ström [16] gives m. p. 101°).

Fraction (ii) was set aside for 7 days at 15° in 10% aqueous methanolic potassium hydroxide (300 c.c.). Dilution with water followed by extraction with ether and careful distillation of the extract gave butanol. The acid fraction solidified slowly; crystallisation from light petroleum (b. p. 40—60°) gave 4-*methylpenta*-2 : 3-*dienoic acid* as small prisms (8·2 g., 7·5% overall), m. p. 80—85°, raised to 89—90° on two further recrystallisations (Found: C, 64·5; H, 7·35%; equiv., 109. $C_6H_8O_2$ requires C, 64·3; H, 7·2%; equiv., 112).

Hydrogenation (0·97 mol.) in ethyl acetate over platinum yielded γ-methylvaleric acid, b. p. 103—105° (bath-temp.)/7 mm., n_D^{15} 1·4181 (Homnelen [17] gives b. p. 199°/752 mm., n_D^{20} 1·4144), identified by conversion into the amide, m. p. 117·5—119·5° (from benzene–light petroleum) (Homnelen [17] gives m. p. 118·5°).

A slow stream of ozonised oxygen was passed through a solution of the acid (0·61 g.) in acetic acid (40 c.c.) at 18° and the emergent gases were washed by passing through a water trap. The water and acetic acid solutions were combined, zinc dust (4 g.) was added, and the mixture distilled in steam. Addition of aqueous 2 : 4-dinitrophenylhydrazine sulphate solution yielded, after three recrystallisations from ethanol, the 2 : 4-dinitrophenylhydrazone of acetone (0·77 g., 60%), m. p. and mixed m. p. 126—127°.

Reaction between Nickel Carbonyl and 3-*Methylpent*-1-*yn*-3-*ol*.—A mixture of dry butanol (80 g.), hydrogen chloride (20 g.), and 3-methylpent-1-yn-3-ol (49 g.) was treated with nickel carbonyl as above. The neutral fraction was isolated with ether, most of the butanol was removed by distillation at atmospheric pressure, and the residue was partially purified by distillation, yielding a pale yellow liquid (36 g.), b. p. 40—60°/0·1 mm. This was hydrolysed with 10% aqueous-ethanolic potassium hydroxide (400 c.c.) at 20° for 5 days; the solution was then acidified and extracted and the extract separated into neutral and acid fractions. Distillation of the former gave 4-*hydroxy*-4-*methylhex*-2-*enoic lactone* (10·1 g., 16%), b. p. 104—105°/17 mm., n_D^{24} 1·4485 (Found: C, 66·7; H, 8·3. $C_7H_{10}O_2$ requires C, 66·6; H, 8·0%). The latter, on distillation, yielded 4-*methylhexa*-2 : 3-*dienoic acid* (11·6 g., 18%), b. p. 92—94°/0·05 mm., n_D^{20} 1·4731 (Found: C, 66·0; H, 7·95%; equiv., 131. $C_7H_{10}O_2$ requires C, 66·6; H, 8·0%; equiv., 126).

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[14] Wotiz and Celmer, *J. Amer. Chem. Soc.*, 1952, **74**, 1860.

[15] Noyes, *ibid.*, 1901, **23**, 395.

[16] Ström, *J. prakt. Chem.*, 1893, **48**, 419.

[17] Homnelen, *Bull. Soc. chim. belges*, 1933, **42**, 243.

Ethyl 4-*Methylpenta*-2 : 3-*dienoate.*—3-Chloro-3-methylbut-1-yne (11 g.) in ethanol (40 c.c.), acetic acid (6 c.c.), and water (1·5 c.c.) was treated with nickel carbonyl (4 c.c.) at 40°. Removal of excess nickel carbonyl, isolation with ether, and separation of the negligible acid fraction left a residue which was distilled, giving ethyl 4-methylpenta-2 : 3-dienoate (3·1 g., 22%), b. p. 99—102°/60 mm., n_D^{18} 1·4580. Alkaline hydrolysis for 20 hr. at 20° gave the acid, m. p. 89—90°, in *ca.* 70% yield.

4-*Methylpenta*-2 : 3-*dienoic Acid* (preferred method).—3-Chloro-3-methylbut-1-yne (10·3 g.) was added slowly to a stirred solution of sodium acetate (16 g.), acetic acid (12 g.—probably unnecessary), water (3 c.c.), and nickel carbonyl (15 c.c.) at 40° during 30 min.; a mildly exothermal reaction took place. After removal of excess of carbonyl, water and ether were added to the cooled mixture; then titration of the aqueous layer with silver nitrate revealed that 90% of the chlorine in the starting material had been liberated. The ethereal extract yielded 4-methylpenta-2 : 3-dienoic acid (3·8 g., 34%), m. p. 85—89°, and its ethyl ester (1·6 g., 11%).

2-*Butylbuta*-2 : 3-*dienoic Acid.*—In the same manner 1-chlorohept-2-yne [18] (10 g.) yielded 2-butylbuta-2 : 3-dienoic acid (4·05 g., 38%) as rhombs, m. p. 68—70° (Wotiz [9] gives m. p. 70°), and the corresponding ethyl ester (1·65 g., 13%), b. p. 86—90° (20 mm.), n_D^{18} 1·4581.

This reaction was examined under varied conditions, with results tabulated.

Buffer	Base (mole)	$Ni(CO)_4$	Time (hr.)	Temp.	Cl^- formed (mole)	Yield (%)
NaOAc–AcOH	1	0·25	0·5	40°	0·25	15
	1	1·0	0·5	40	0·96	43
	1	1·0	0·5	40	0·89	40
	1	1·0	16	20	0·45	23
	2	1·0	0·5	40	0·89	42
Na_2HPO_4–NaH_2PO_4 ...	1	1·0	0·5	40	—	9·5

The poor result with the phosphate buffer may be due to the poor solubility of these salts in the aqueous-alcoholic solvent.

Buta-2 : 3-*dienoic Acid.*—3-Chloroprop-1-yne [19] (6·7 g.), ethanol (30 c.c.), acetic acid (5·4 g.), sodium acetate (7·4 g.), and water (1·5 c.c.) were treated with nickel carbonyl (3·5 c.c.) at 60°. No exothermal reaction ensued. Isolation of the acid fraction gave an oil which failed to solidify and was sublimed at 50°/0·05 mm., yielding, after crystallisation from light petroleum (b. p. 40—60°), the acid (0·5 g., 6%) as plates, m. p. 60—62°, undepressed on admixture with an authentic sample prepared by the method of Eglinton *et al.*[10]

Hepta-2 : 3-*dienoic Acid.*—3-Chlorohex-1-yne [20] (11·7 g.), ethanol (30 c.c.), acetic acid (6 g.), sodium acetate (8·2 g.), and water (1·5 c.c.) were treated with nickel carbonyl (4 c.c.) in ethanol (5 c.c.). After isolation with ether, distillation yielded the *acid* (1·3 g., 10%), b. p. 86—90°/0·2 mm., n_D^{18} 1·4842 (Found: C, 66·8; H, 7·9. $C_7H_{10}O_2$ requires C, 66·6; H, 8·0%). It formed an amide (prepared *via* the acid chloride) which crystallised from benzene–light petroleum in rosettes of needles, m. p. 108—111°, and absorbed strongly at 1960 cm.$^{-1}$. Hydrogenation in ethyl acetate over platinum (uptake 97%) yielded *n*-heptanoic acid, identified by conversion into its amide, m. p. 95—96° (Robertson [21] gives m. p. 96°).

2-*Butyl*-4-*methylpenta*-2 : 3-*dienoic Acid.*—2-Chloro-2-methyloct-3-yne [22] (16 g.), ethanol (30 c.c.), acetic acid (6 g.), sodium acetate (8·2 g.), and water (1·5 c.c.) were treated with nickel carbonyl (4 c.c.). A mildly exothermal reaction occurred; isolation of the acid fraction followed by crystallisation from light petroleum (b. p. 40—60°) gave the acid as acicular prisms (2·15 g., 13%), m. p. 75—76° (Wotiz and Palchak [23] give m. p. 77—78°).

3-*Chlorobut*-1-*yne* (with J. M. THOMPSON).—A mixture of but-3-yn-2-ol (44 g.), pyridine (50 c.c.), and dry ether (60 c.c.) was added dropwise to a stirred solution of thionyl chloride (81 g.; freshly redistilled) in dry ether (60 c.c.) during 30 min. After 16 hours' stirring at 20°, water (200 c.c.) was added and the ethereal layer was separated and washed with sodium carbonate solution and water. Distillation of the dried ethereal solution through a 10 cm. Fenske column gave the *chloride* (23 g., 42%), b. p. 69°/758 mm., n_D^{18} 1·4256 (Found: C, 54·2; H, 6·0. C_4H_5Cl requires C, 54·25; H, 5·65%).

Penta-2 : 3-*dienoic Acid.*—3-Chlorobut-1-yne (8 g.) was added to a stirred and warmed

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[18] Newman and Wotiz, *J. Amer. Chem. Soc.*, 1949, **71**, 1295.
[19] Hatch and Chiola, *ibid.*, 1951, **73**, 361.
[20] Hennion and Sheehan, *ibid.*, 1949, **71**, 1965.
[21] Robertson, *J.*, 1919, 1220.
[22] Campbell and Eby, *J. Amer. Chem. Soc.*, 1940, **62**, 1799.
[23] Wotiz and Palchak, *ibid.*, 1951, **73**, 1972.

mixture of ethanol (60 c.c.), sodium acetate (15·1 g.), acetic acid (10·8 g.), water (2·5 c.c.), and nickel carbonyl (14 c.c.). No exothermal reaction ensued, the temperature was kept at 40° for 30 min., and the mixture was worked up. A chloride estimation on the aqueous layer indicated 92% of the theoretical amount. On distillation the acid fraction, b. p. 51°/0·05 mm., rapidly solidified, and crystallisation from light petroleum (b. p. 40—60°) then gave the *acid* as needles (1·1 g., 12·5%), m. p. 38—40° (Found: C, 60·75; H, 6·2. $C_5H_6O_2$ requires C, 61·2; H, 6·15%).

4-*Phenylbuta*-2 : 3-*dienoic Acid*.—3-Chloro-3-phenylprop-1-yne [24] (15·1 g.) was added to a stirred mixture of ethanol (30 c.c.), acetic acid (6 g.), sodium acetate (8·2 g.), water (1·5 c.c.), and nickel carbonyl (4 c.c.) at 40°. A mildly exothermal reaction ensued and after removal of excess of nickel carbonyl by co-distillation the mixture was poured into water and extracted with ether. After extraction with sodium carbonate solution the aqueous layer was brought to pH 7 with hydrochloric acid, which liberated a polymeric mass. Removal of the latter by filtration was followed by acidification to pH 1 and ether-extraction. Evaporation of the dried extract and crystallisation of the residue from light petroleum (b. p. 40—60°)–ether gave the *acid* as rhombs (1·9 g., 12%), m. p. 94—96° (Found: C, 75·25; H, 5·3. $C_{10}H_8O_2$ requires C, 75·0; H, 5·05%).

Hydrogenation in ethyl acetate over platinum (uptake 95%) gave γ-phenylbutyric acid, m. p. 46—48° after two recrystallisations from water (Overbaugh, Allen, Martin, and Fieser [25] give m. p. 47—48°).

THE UNIVERSITY, MANCHESTER, 13.
THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

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[24] Levy and Cope, *J. Amer. Chem. Soc.*, 1944, **66**, 1687.

[25] Overbaugh, Allen, Martin, and Fieser, *Org. Synth.*, 1935, **15**, 64.